Stiff, porous scaffolds from magnetized ceramic particles aligned by magnetic freeze casting

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ABSTRACT

Bone consists of a hard mineral phase and a compliant biopolymer phase resulting in a composite material that is both lightweight and strong. Osteoporosis that degrades spongy bone preferentially over time leads to bone brittleness in the elderly. A porous ceramic material that can mimic spongy bone for a one-time implant provides a potential solution for the future needs of an aging population. Scaffolds made by magnetic freeze casting resemble the aligned porosity of spongy bone. A magnetic field applied throughout freezing induces particle chaining and alignment of lamellae structures between growing ice crystals. After freeze drying to extract the ice and sintering to strengthen the scaffold, cubes from the scaffold center are mechanically compressed along longitudinal (z-axis, ice growth direction) and transverse (y-axis, magnetic field direction) axes. The best alignment of lamellar walls in the scaffold center occurs when applying magnetic freeze casting with the largest particles (350 nm) at an intermediate magnetic field strength (75 mT), which also agrees with stiffness enhancement results in both z and y-axes. Magnetic moments of different sized magnetized alumina particles help determine the ideal magnetic field strength needed to induce alignment in the scaffold center rather than just at the poles.

KEYWORDS: freeze casting, ferrofluid, magnetic alignment, ceramic scaffold, mechanical properties

1. INTRODUCTION

Gravity and electromagnetism are natural forces responsible for celestial body assembly in the universe. On a much smaller scale, Earth's magnetic field plays some role in "biological body" assembly, or how living organisms orient themselves with respect to their surrounding environment [1]. Biogenic magnetite (Fe_3O_4) has been found in sharks [2], pigeons [3], honeybees [4], humans [5], and most notably in magnetotactic bacteria that align parallel to the earth's magnetic field direction in search of microaerophilic regions of low oxygen concentration [6]. These bacteria have single domain Fe_3O_4 crystals packaged within organelle magnetosomes that form a chain along the long axis of the bacteria. This magnetic sensing capability imparted by magnetosome alignment within magnetotactic bacteria provides an interesting avenue for bioinspired applications using anisotropically aligned materials that resemble naturally ordered structures.

Strong magnetic fields ($\approx 9\text{-}18\text{ T}$) have been used along with a slip casting process to finely control and texture anisotropic ceramic particles to improve their physical, chemical and mechanical properties [7-15]. Particles in a slurry with weak anisotropic magnetic susceptibility can rotate within a strong magnetic field to an angle that minimizes the system energy. Macroscopic alignment occurs when the magnetic energy on rotation exceeds the thermal energy for the slurry particles. The degree of particle orientation depends on several processing factors in addition to the strong magnetic field, such as heating temperature, particle size and suspension viscosity [10]. Recently, magnetic slip casting has been used at much lower magnetic field strength ($< 40\text{ mT}$) to manipulate surface magnetized alumina (Al_2O_3) platelets [16]. Fine control over these magnetized materials has led to reinforced composites [17-20], self-shaping composites [21], tunable fluorescence emission [22], and additive manufacturing processes such as 3D magnetic printing [23, 24].

Mimicking the complex microstructures of natural materials provides a new challenge for further exploration. A common design theme from a widely studied natural material, bone, is the hierarchical organization of nanomaterials (grains, platelets or fibers) that when combined in a controlled manner, form a high strength and high toughness composite [25]. Bone is a multifunctional composite that must be strong to support the body, tough to absorb impact forces, lightweight to enable movement, and porous to replenish nutrients [26, 27]. Cortical bone provides a dense outer sheath while the interior trabecular bone enables marrow production and cell growth within the large interconnected pores of the spongy bone interior [27]. Pore alignment in load bearing regions is an important design feature along with prevention of pore expansion due to osteoporosis [28]. Fabrication

of aligned porous structures that resemble trabecular bone necessitates methods that can provide dual levels of control over structural features with disparate length scales and along multiple directions.

Freeze casting is a physical process that uses an aqueous slurry consisting of a particulate solid phase (e.g., ceramic particles) and a freezing agent (e.g., water) [29-33]. Bulk macrostructures can be modulated via ice templated crystal growth that separates particles into lamellar structures aligned along the freezing direction (z-axis). Following a freeze drying step to remove the ice crystals, the porous scaffold consisting of lamellar walls interconnected by particle bridges is sintered to strengthen the overall structure. The quantity and dimension of the pores and the overall architecture can be modified by adjusting the solid loading [34, 35], changing the liquid freezing agent [36-38], and introducing additives [39-42]. Although the scaffolds are typically strong in the ice growth direction, the transverse properties are generally poor. Non-invasive methods for strengthening scaffolds along the transverse direction (y-axis) normal to the freezing direction are promising next steps.

Various freeze casting techniques have been developed for scaffold pore alignment [43-46], however, Porter, *et al.* [47-49] were the first to apply magnetic fields during the freeze casting process. Various applied magnetic field orientations on slurry mixtures of ceramic particles and ≈ 9 wt.% Fe_3O_4 particles (≈ 50 nm) mechanically enhanced scaffold properties normal to the ice growth axis. Most notably, titania (TiO_2) and Fe_3O_4 slurry mixture showed weak interactions between both components when subjected to a transverse magnetic field (≈ 120 mT) that served to align lamellar walls and strengthen the scaffold structure under compression along the magnetic field axis [47]. TiO_2 is a paramagnetic material with a weak positive magnetization and susceptibility that varies only at very low temperature (< 100 K) or at a very high applied magnetic field. In another study, zirconia (ZrO_2) and Fe_3O_4 slurry mixtures were subjected to a rotating magnetic field (≈ 120 mT) that produced a banded helical structure with enhanced torsional properties [48]. Recently, a transverse magnetic field (≈ 90 mT) applied to a ZrO_2 and Fe_3O_4 slurry mixture formed aligned mineral bridges with enhanced mechanical properties along the magnetic field axis [49]. Different from the TiO_2 mixtures [47], the ZrO_2 mixtures [48, 49] did not show substantial interparticle interactions between the ZrO_2 and Fe_3O_4 phases, which led to distinct separation of the phases, and subsequently, the helical or bridge-like features.

Below a critical diameter (≈ 120 nm), Fe_3O_4 exists in a single domain state whereby all spins align uniformly in an applied magnetic field direction [50]. Superparamagnetism occurs in smaller Fe_3O_4 particles (< 15 - 20 nm) as a super moment that can easily flip in response to a changing magnetic field. This behavior is due to the particle thermal energy ($k_B T$, Boltzmann's constant $\cdot$ temperature) exceeding the magnetic anisotropy energy barrier ($K_{eff} V$, anisotropy constant $\cdot$ particle volume) that

typically fixes magnetic moments in place along a particular direction. Superparamagnetic Fe₃O₄ is therefore quite different from larger particles made up of ferromagnetic (elemental iron, nickel, cobalt) or ferrimagnetic (oxides of iron, nickel, cobalt) materials that behave like permanent magnets regardless of an applied magnetic field.

Superparamagnetic Fe₃O₄ used in concert with non-magnetic materials has low magnetic field applications. Dynabeads® (Thermo Fisher Scientific, Waltham, MA) comprise a core of superparamagnetic Fe₃O₄ surrounded by a polystyrene shell. These composites respond even at low magnetic field strength and are often functionalized for magnetically controlled separation applications [51]. Recently, researchers surface magnetized ceramic particles with ferrofluid [17], which consists of a stable suspension of superparamagnetic Fe₃O₄ particles (≈ 10 nm) coated with a stabilizing dispersing agent (surfactant) in a liquid carrier. The surfactant charge has a dual purpose for preventing Fe₃O₄ particle agglomeration in the ferrofluid and facilitating electrostatic adsorption of Fe₃O₄ to the ceramic particle surface. Ceramic particles in water have a point-of-zero charge (PZC), which is the pH when the surface becomes electrostatically neutral [52], and water molecules hydroxylate the surface to become protonated or deprotonated according to the Gouy-Chapman theory [53]. For example, Al₂O₃ (PZC ≈ 9) [54] in water (PZC ≈ 7) becomes protonated and superparamagnetic Fe₃O₄ particles, coated with anionic surfactant, electrostatically adhere to magnetize the surface of the larger, non-magnetic material.

Equations that describe chain formation of single domain Fe₃O₄ (≈ 50 nm) in magnetosomes of magnetotactic bacteria [55] can be used to predict how isolated superparamagnetic Fe₃O₄ particles [56] and Dynabeads® [57, 58] in water respond to a magnetic field gradient. For non-magnetic materials surface magnetized with sparsely attached superparamagnetic Fe₃O₄, particle-particle magnetic interaction is described by the ratio between particle interaction energy (U) and thermal energy ($k_B T$) to obtain a unitless magnetic coupling parameter (Γ), according to the following equations:

$$U = \frac{\mu_0 m^2}{4\pi d^3} [1 - 3 \cos^2 \theta] \quad (1)$$

$$\Gamma = \frac{U}{k_B T} = \frac{\mu_0 m^2}{2\pi d^3 k_B T} \quad (2)$$

where μ_0 is the magnetic permeability of free space ($4\pi \times 10^{-7}$ H/m), m is the particle magnetic moment dipole, d is the center-center interparticle distance (equal to one particle diameter for particles touching in a chain) and θ is the angle between the external magnetic field direction and the line that connects between the centers of two particles.

The equation for Γ stipulates that a minimum energy configuration exists at $\theta = 0^\circ$. The inset in Figure 1 shows how the formation of highly anisotropic, aligned assemblies in solution occurs due to

magnetic dipole-dipole interaction energy between particles at strongly attractive regions where $\theta \approx 0^\circ$ (vertical, indicated in red), instead of at strongly repulsive regions where $\theta > 54.7^\circ$ (horizontal, indicated in green)[57]. Particle-particle interactions for colloidal stability are described by classical DLVO theory [59] that includes attractive van der Waals forces and repulsive electrostatic forces. Generalization of DLVO theory to include magnetic interaction leads to a theoretical overall free energy profile of interaction between two electrostatically stable particles [57, 60, 61]. The electrostatic repulsion responsible for particle stabilization creates an energy barrier between a deep primary minimum (due to van der Waals attraction) and a shallow secondary minimum (due to magnetic interaction energy), as shown in Figure 1. The depth of the secondary minimum depends on the value of Γ . Particles captured in the secondary minimum aggregate to form chains in the presence of a magnetic field gradient due to a sufficiently large magnetic interaction energy. The secondary minimum disappears when the magnetic field is removed and the particles redisperse within the liquid medium without addition of energy.

Figure 1. Free energy profile diagram of interaction between electrostatically stabilized spherical particles that have been surface magnetized with superparamagnetic particles and subjected to a strong magnetic field. Assumptions applied from a generalized DLVO theory include a deep primary minimum (van der Waals attraction), an energy barrier (electrostatic repulsion) and a secondary minimum (magnetic interaction, vertical, indicated in red) where chain formation occurs according to the magnetic coupling parameter (Γ) value. Repulsive regions (horizontal, indicated in green) exist on the sides due to the particle dipole (up arrow, indicated in orange) oriented in the magnetic field direction.

This reversible chaining of superparamagnetic Fe_3O_4 in combination with non-magnetic materials has diverse applications besides its use in polymer coated Dynabeads® for magnetic separation. A value of $\Gamma \gg 1$ corresponds to a system dominated by magnetic interactions with particle chain formation, whereas $\Gamma \ll 1$ results in no particle chaining due to a preponderance of thermal agitation. However,

chain formation is not easily predictable in experimental systems with values close to $\Gamma \approx 1$ for superparamagnetic particles alone [56, 57] or when surrounded by non-magnetic material. For example, previous work on superparamagnetic Fe_3O_4 surrounded by a silica shell ($\Gamma = 3.5$) did not form particle chains, although this was suggested to have been due to leftover capping agent that could have had a significant impact on the observed result [62]. Magnetic freeze casting with surface magnetized ceramic particles provides an alternative avenue for experimental validation of particle chain formation from measurement of Γ and mechanical characterization of sintered scaffolds.

This work investigates a new method for making multi-axis strengthened porous structures that resemble trabecular bone by magnetic freeze casting with surface magnetized Al_2O_3 particles. The magnetic field strength needed to align lamellar walls for stiffness enhancement in the transverse direction is explored. The magnetization method applied here provides better control over smaller superparamagnetic Fe_3O_4 electrostatically adsorbed to the larger Al_2O_3 particle surface. Any structural materials that respond either weakly (e.g., TiO_2) or not at all (e.g., ZrO_2 , Al_2O_3 , hydroxyapatite) to a magnetic field can be surface magnetized, thus control over macro and microstructures by magnetic freeze casting can provide a feasible pathway towards construction of dynamic material systems that sense, interact with and even adapt to the surrounding environment [63].

2. MATERIALS AND METHODS

2.1 Particle Surface Magnetization

Three different $\alpha\text{-Al}_2\text{O}_3$ particles (BMA15, 150 nm; SM8, 350 nm; CR6, 500 nm; particle size estimated by supplier Baikowski, Malakoff, TX, USA) were surface magnetized, as shown in Figure 2. For each particle size, 2.5 g Al_2O_3 was stirred in 75 mL distilled water, while 100 μL of anionic ferrofluid (EMG-705, Ferrotec, Bedford, NH, USA) was diluted in 5 mL distilled water in a separate container and dropwise added to the stirring Al_2O_3 solution. After stirring for 12 hours, white colored Al_2O_3 particles changed to a light brown color and the surrounding solution became clear. Residual anionic surfactant was rinsed off from magnetized particles with distilled water and vacuum filtration. The magnetized Al_2O_3 was then dried for 12 hours at 100°C before use in magnetic freeze casting slurries.

Figure 2. Preparation of magnetized alumina particles. **(a)** Ferrofluid consisting of magnetite (≈ 10 nm) nanoparticles coated with an anionic surfactant was diluted and dropwise added to a stirring alumina slurry. **(b)** Non-magnetic alumina particles (left) became magnetized (right) after stirring for 12 hours. **(c)** Scanning electron micrograph of magnetized alumina particles (≈ 350 nm) with magnetite on the surface.

2.2 Magnetized Slurry Preparation

Magnetized Al_2O_3 particle slurries (10 vol.%) were prepared (by weight Al_2O_3) with polymer binders 1 wt.% polyvinyl alcohol (PVA, 100,000 g/mol molecular weight (MW), Alfa Aesar, Ward Hill, MA, USA), 1 wt.% polyethylene glycol (PEG, 10,000 g/mol MW, Alfa Aesar, Ward Hill, MA, USA) and 1 wt.% anionic dispersant (Darvan 811, R. T. Vanderbilt Company, Inc., Norwalk, CT, USA). Al_2O_3 grinding media was added to the slurry and the mixture was ball milled for 24 hours. After milling, particle sizes, measured at least twenty times by the dynamic light scattering (DLS) technique (Microtrac Nanotrak Wave II, Montgomeryville, PA), provided a number distribution of the mean particle diameter [64-66].

2.3 Magnetic Freeze Casting

A vise grip (Panavise, Reno, NV) with ≈ 420 mT bar magnets (N52 grade, K&J Magnetics, Inc. Pipersville, PA, USA) attached to either end allowed for a static magnetic field apparatus that was adjustable. A handheld Gauss meter measured the magnetic field strength at the gap, located at the midpoint between the magnets. An exponential curve fit from the data points was acquired at successively increasing 5 mm gap intervals, yielding an equation for conversion of gap distance to magnetic field strength. The Gauss meter measurements closely resembled calculated values for two disc magnets attached to an iron yoke, as shown in Figure 3. Freeze casting with magnetized

Al_2O_3 subjected to no magnetic field versus a static transverse magnetic field ($\approx 25, 75, 150 \text{ mT}$) was accomplished in a polyvinyl chloride (PVC) mold. A groove was filed along the inside wall of the mold and aligned perpendicular to the magnetic field axis to provide a visual indicator where the magnetic field was applied on the sintered samples.

Figure 3. Gap magnetic field strength determination via theoretical calculation and measurement. Plotted red squares indicate calculated magnetic field strength at increasing gap distances for two disc magnets attached to an iron yoke. Plotted black circles and trend line indicate measured magnetic field strength at increasing gap distances with a Gauss meter at the center point between bar magnets.

Each surface magnetized Al_2O_3 slurry was degassed under low vacuum for 15 minutes before pouring 5 mL into the PVC freeze cast mold. The static magnetic field apparatus was situated and centered on the PVC mold, as shown in [Figure 4a](#). Directional freezing occurred from the bottom upward using a custom built freeze casting device, as previously described [\[47\]](#). Frozen solid samples were lyophilized with a bench-top freeze dryer (Labconco, Kansas City, MO, USA) at -50°C and $3.5 \times 10^{-6} \text{ Pa}$ for 48 hours. Ice crystals sublimed leaving behind fragile ‘green body’ scaffolds composed of particles held together by the polymer binders. Samples were sintered in an open air furnace for 3 hours at 1500°C with heating and cooling rates of $2^\circ\text{C}/\text{min}$, following a procedure that provided reproducible results with uniform porosity [\[47\]](#).

Figure 4. Magnetic freeze casting setup and sintered scaffold cube compression diagram. **(a)** Ice crystals grow along the *z*-axis while a static magnetic field is applied along the *y*-axis. **(b)** Mechanical properties are compared via cubes from the center of the sintered scaffold compressed in the ice growth direction (*z*-axis, blue cube face) and the magnetic field direction (*y*-axis, orange cube face).

2.4 Materials Characterization

Magnetized Al_2O_3 particles ($\approx 15\text{-}30$ mg) were characterized with a vibrating sample magnetometer (VSM, VersaLab, Quantum Design International, San Diego, CA, USA) with moment measured in response to a sweeping magnetic field (0-3000 Oe). Mass magnetization (M , Am^2/kg) and particle magnetic moment (m , Am^2) was calculated from magnetometer measurements coupled with particle volume (v) measured by DLS, according to the following equations:

$$M = \text{moment} / \text{sample weight} \quad (3)$$

$$m = v \times M \quad (4)$$

Sintered scaffolds sectioned at midpoint height were mounted to a stage and coated with colloidal graphite along the bottom and side walls. Iridium was sputter coated (EMITech K575X, Quorum Technologies Ltd., West Sussex, UK) for 15 s at 85 mA onto the top. Scanning electron microscopy (SEM) micrographs at 10 kV (spot size 3 nm) from a Philips XL30 field emission environmental scanning electron microscope (FEI-XL30, FEI Company, Hillsboro, OR) was used to characterize scaffold pore dimensions. Image analysis with ImageJ software (National Institutes of Health, Bethesda, MD, USA) maintained a contrast threshold at a consistent value in all micrographs. An ellipse fit to each measured pore provided dimensions for the major axis (a) and minor axis (b). For each scaffold, 40 individual pores were measured to obtain pore area ($A_p = \pi ab/4$) and lamellar wall thickness (t), which was how other scaffolds were analyzed in previous work [41, 42].

2.5 Mechanical Characterization

Compression testing of sintered Al_2O_3 scaffolds was performed on a 3342 Instron materials testing machine (Instron, Norwood, MA) with a 500 N static load cell at a crosshead velocity of 0.005 mm/s. Two samples ($\approx 5 \text{ mm}^3$ cubes) cut from each scaffold center (Figure 4b) were compressed, one in the ice growth direction (z-axis) and the other in the magnetic field direction (y-axis). Ultimate compressive strength and Young's modulus were determined from the maximum stress and linear slope of the stress–strain curves, respectively.

3. RESULTS AND DISCUSSION

3.1 Magnetic Response of Magnetized Alumina Particles

Al_2O_3 particle sizes were estimated by the supplier to be 150 nm (BMA15), 300 nm (SM8) and 500 nm (CR6), however, average particle sizes measured by DLS after ball milling were actually 195 nm, 225 nm and 350 nm, respectively, as shown in Figure 5. Equal weights of different sized Al_2O_3 particles were magnetized with equal volumes of ferrofluid to ensure equal amounts of surface adsorbed Fe_3O_4 . VSM measurements converted to particle magnetic moment, m , (Eqns. 3, 4) showed a correlation with particle size (Figure 6). Since Γ is proportional to m^2 (Eqn. 2), larger particles were more likely to overcome thermal agitation dominance and Brownian motion compared with smaller particles [57].

Figure 5. Dynamic light scattering measurement of alumina particle sizes. Each particle type was segmented into a mean number distribution that consisted of particle percentage at different particle size bins and plotted for comparison. The product of each particle percentage with corresponding bin size was summed to determine the reported mean for each particle type.

Figure 6. Comparison of particle magnetic moment, m , determined from magnetometer measurements for different sized magnetized alumina particles. The value m is squared in the numerator of Eqn. 2 and is the product of the measured magnetic moment, density and spherical particle volume divided by the sample weight. Larger magnetized alumina particles have greater values for m than smaller particles.

DLS measured average Al_2O_3 particle size, d , and VSM measured moment, m , were combined in Eqn. 2 to obtain Γ as a function of applied magnetic field strength (left side, Figure 7a-c). For each average

particle size, Γ fell below the threshold ($\Gamma > 1$) predicted for particle chaining when magnetic interaction energy exceeds thermal agitation. Since average particle size poorly represents the actual size disparity evident in a mean number distribution for each Al_2O_3 particle type (Figure 5), Γ was recalculated to determine percent for each particle type above the threshold ($\Gamma > 1$) at a magnetic field strength of 75 mT (right side, Figure 7a-c). The 195, 225 and 350 nm particles had 8%, 11% and 20% of each type above the threshold ($\Gamma > 1$) at 75 mT, respectively, while 16%, 25% and 33% were above the same threshold at 150 mT, respectively.

Figure 7. Comparison of the calculated magnetic coupling parameter (Γ) values and mean number distribution of particle sizes for different sized alumina particles. Values above $\Gamma \approx 1$ were not evident at any magnetic field strength for (a) 195 nm, (b) 225 nm or (c) 350 nm particles. A higher percentage of larger particles within the DLS measured mean number distribution for 350 nm particles had values above $\Gamma \approx 1$.

3.2 Lamellar Wall Alignment

During the time before freezing started, magnetized particles subjected to an applied magnetic field likely underwent particle chaining in a manner similar to previously reported 1D chain formation of Fe_3O_4 nanoclusters at room temperature in aqueous solution [67]. A slurry temperature of 298 K was used in Eqn. 2 for the calculated Γ values (Figure 7), which underestimated Γ by $\approx 10\%$ because T was ≤ 273 K just before freezing actually occurred. Chaining between the percent of larger slurry particles above the threshold ($\Gamma > 1$) likely contributed to guiding the formation of lamellar walls aligned between growing ice crystals. Mineral bridges made up of particles trapped within the growing ice front could then connect between adjacent lamellae in a similar fashion as in normal freeze casting.

Figure 8. Scanning electron micrographs of scaffold center regions for different sized magnetized alumina particles after magnetic freeze casting at 0, 25, 75 and 150 mT. **(a)** 195 nm alumina particles did not exhibit lamellar wall alignment at any of the applied magnetic fields, while **(b)** 225 nm alumina particles had limited alignment at 150 mT. **(c)** 350 nm alumina particles had lamellar wall alignment that was most evident at **(d)** 75 mT, however, at **(e)** 150 mT there was disordered alignment likely due to flux field effects. **(f)** Closer examination of the scaffold microstructures shows mineral bridge formation and **(g)** particles sintered together within lamellar walls aligned along the magnetic field axis.

In [Figure 8](#), SEM micrographs from the center of the scaffolds show transverse cross-sections perpendicular to the ice growth direction([Figure 8a-c](#)). As expected for each particle size, no lamellar wall alignment occurred during freeze casting when there was no applied magnetic field. All of the magnetic field conditions for 195 nm scaffolds indicated no alignment of lamellar walls along the magnetic field axis ([Figure 8a](#)). Some regions of lamellar wall alignment were evident for 225 nm scaffolds at 150 mT, but none at lower strength magnetic fields ([Figure 8b](#)). For 350 nm scaffolds ([Figure 8c](#)), more lamellar wall alignment was evident at 75 mT ([Figure 8d](#)) than at 150 mT ([Figure 8e](#)). Image analysis of stitched together SEM micrographs (6 mm × 2.7 mm) from the center of 350 nm scaffolds indicated ≈20% lamellar wall alignment at 75 mT and ≈12% alignment at 150 mT (results not shown). Interestingly, calculation of particle chaining percentage from DLS measured particle size (d) and VSM measured moment (m) above the threshold ($r > 1$), for 350 nm slurries at 75 mT, was actually borne out by lamellar wall alignment in the scaffold center, although not at 150 mT. This result indicates that a sufficient, but not excessive, amount of applied magnetic field strength is necessary to align lamellar walls in the scaffold center. High magnification SEM micrographs of 350 nm scaffolds show lamellar wall alignment and mineral bridge formation at 75 mT ([Figure 8f,g](#)) along the (horizontal) magnetic field axis.

Different sized Al_2O_3 particles in this study produced scaffolds with similar porosity ($\approx 80\text{-}85\%$, [Table 1](#)) and lamellar wall thickness (2.3–3 μm , [Table 1](#)) as previous freeze casting work with ZrO_2 [[35](#)] and TiO_2 [[41](#)] that had the same processing conditions. However, the pore area for the Al_2O_3 scaffolds (35–45 μm^2 , [Table 1](#)) was more than 20x and 5x smaller than for ZrO_2 [[35](#)] and TiO_2 [[41](#)] scaffolds, respectively, despite Al_2O_3 particles having similar sizes as ZrO_2 and TiO_2 particles. Molecular dynamic simulations indicate material properties (e.g., surface morphology, hydrophobicity, lattice mismatch) [[68](#)] and particle surface modification with adsorbed molecules can significantly increase or decrease ice nucleation rate [[69](#)], which can explain this discrepancy. For the case of freeze casting at a slower cooling ramp (5°C/min) with a wide range of Al_2O_3 sizes (0.2–3.4 μm), Deville, *et al.* [[70](#)] speculated that smaller particles with higher surface area had more ice nucleation sites that led to scaffolds with larger pore area and lamellar wall thickness. For this study, a much narrower size range of Al_2O_3 particles likely mitigated any large difference between number of nucleation sites, although pore area and lamellar wall thickness slightly increased for larger magnetized Al_2O_3 particles ([Table 1](#)). Altered ice nucleation rates in other freeze casting systems using different solidification rates, materials, particle sizes and unmodified surfaces can further complicate comparison of measured scaffold properties. Additional experimental

work on heterogeneous ice nucleation is certainly needed to correlate empirical results with fundamental understanding of physiochemical processes from molecular dynamics simulations [68].

Table 1. Porosity, pore area and lamellar wall thickness of alumina particle scaffolds freeze cast at various static magnetic fields (0, 75, 150 mT). Sample size for each condition: $N = 6$. All data reported are mean $\pm$ standard error (standard deviation / $\sqrt{N}$).

	Magnetic field strength (mT)	195 nm particles	225 nm particles	350 nm particles
Porosity (%)	0	83.74 $\pm$ 0.15	83.35 $\pm$ 0.17	82.60 $\pm$ 0.19
	75	84.77 $\pm$ 0.29	83.44 $\pm$ 0.18	82.33 $\pm$ 0.18
	150	85.29 $\pm$ 0.11	81.60 $\pm$ 0.33	81.83 $\pm$ 0.58
Pore area (μm^2)	0	37.28 $\pm$ 2.57	41.20 $\pm$ 2.56	43.33 $\pm$ 2.92
	75	37.82 $\pm$ 2.38	38.12 $\pm$ 2.17	47.29 $\pm$ 3.50
	150	34.64 $\pm$ 2.21	41.97 $\pm$ 2.69	42.54 $\pm$ 2.53
Lamellar wall thickness (μm)	0	2.32 $\pm$ 0.05	2.53 $\pm$ 0.06	2.85 $\pm$ 0.07
	75	2.31 $\pm$ 0.07	2.58 $\pm$ 0.07	2.91 $\pm$ 0.08
	150	2.34 $\pm$ 0.09	2.56 $\pm$ 0.08	3.04 $\pm$ 0.08

Application of a low magnetic field to align magnetized Al_2O_3 particle chains within lamellar walls was primarily responsible for strengthening the scaffold along the transverse magnetic field axis. Recently, magnetic freeze casting used with slurries of 10 vol.% ZrO_2 mixed with 50 nm Fe_3O_4 particles showed mineral bridge alignment and thickness increased as Fe_3O_4 content and transverse magnetic field strength increased [49]. In those slurry mixtures, larger Fe_3O_4 particles with ferromagnetic properties ($r \gg 1$) led to particle chaining of Fe_3O_4 concentrated within aligned and thickened mineral bridges along the transverse magnetic field axis. In the present study, slight thickening of the lamellar walls occurred at varying magnetic field strength for 350 nm particles only (Table 1), resulting in mostly uniform microstructures compared with those presented in previous work.

3.3 Mechanical Properties

The porosity for scaffolds freeze cast from a slurry of 10 vol.% Al_2O_3 was consistent across all samples (≈ 80 -85%), so direct comparison of mechanical properties could be correlated between particle sizes. At no applied magnetic field, pore area and lamellar wall thickness increased with particle size (Table 1). Figure 9a shows a representative y-axis stress-strain curve for the 350 nm scaffolds prepared with and without an applied magnetic field. The large uneven plateau region on the plot is typical of porous materials, where individual walls are fracturing over a large strain range. It is clear that the Young's modulus (E) and ultimate compressive strength (UCS) are larger with the application of a

magnetic field, corroborating the results of Porter, *et al.* [47] who found the same effect in TiO₂ scaffolds. Figure 9b,c summarizes E and UCS in the y -axis (magnetic field direction) and z -axis (ice growth direction) as a function of particle size and magnetic field strength. In Figure 9b, E and UCS in the y -axis ranged between ≈ 30 -90 MPa and ≈ 1.2 -2.8 MPa, respectively. In general, both E and UCS increased with increasing particle size, which is attributable to scaffolds with larger particles having thicker lamellar walls. For 225 nm scaffolds, E increased by $\approx 50\%$ at 150 mT compared to ones prepared at 0 mT (Figure 9b), while E was not enhanced at any magnetic field strength for 195 nm scaffolds. The 350 nm scaffolds prepared at 75 mT had the highest E increase by $\approx 100\%$ compared to ones prepared at 0 mT (Figure 9b), which correlated well with enhanced lamellar wall alignment observed in SEM micrographs. During processing at 150 mT, it is likely that the magnetic flux lines were not parallel throughout the sample, but displayed some curvature, as found in finite element models for the flux lines [49]. The lower E value at 150 mT is attributable to the curvature of the magnetic flux in the scaffold center, which caused misalignment of the lamellar walls. These results demonstrate that particle sizes < 350 nm show no or limited effect on y -axis properties when having a magnetic field applied during solidification.

Figure 9. Comparison of compressive mechanical properties with stress-strain curve, modulus and strength values for porous scaffolds of magnetized alumina particles prepared by magnetic freeze casting. (a) A representative stress-strain curve for 350 nm particles made with no magnetic field (dotted line) and static magnetic field of 75 mT (solid line). Compressive Young's modulus and ultimate strength as a function of particle size and magnetic field strength in the (b) magnetic field (y -axis) and (c) ice growth direction (z -axis). Data points are the mean of $N = 6$ measurements with error bars representing $\pm$ standard error (standard deviation / $\sqrt{N}$).

Figure 9c shows that E and UCS in the z-axis ranged between ≈ 100 -260 MPa and ≈ 10 -21 MPa, respectively. Both E and UCS values were much greater than in the magnetic field direction because more lamellar wall alignment occurred in the ice growth direction. In general, both E and UCS increased with particle size in the z-axis, again due to the increase in lamellar wall thickness (Table 1). For 350 nm scaffolds, more so than for 195 nm or 225 nm scaffolds, increased magnetic field strength produced ordered regions of lamellar walls oriented parallel to each other in “grains” along axes transverse to the freezing direction. Generally, scaffold compression along the z-axis causes crack formation and growth to occur due to local buckling of lamellar walls. However, for 350 nm scaffolds subjected to increased magnetic field strength, the compressive load was distributed more evenly by ordered regions of aligned walls (“grains”) with mineral bridges between parallel lamellae that prevented Euler buckling by hindering crack propagation [39, 41]. In both y and z-axes, E was a more reliable indicator of scaffold strengthening than the UCS. Consistent trends for UCS were not evident in the y or z-axes for scaffolds of any particle size at increased magnetic field strength due to variable defects that can have a large impact during mechanical compression.

Previous work demonstrated enhancement of E and UCS due to lamellar wall alignment along the y-axis for a slurry mixture of TiO_2 mixed with ferromagnetic Fe_3O_4 (≈ 50 nm) at an applied magnetic field of 120 mT [47]. Similar improvement in the y-axis was evident for ZrO_2 and Fe_3O_4 at 90 mT, although mineral bridges were aligned rather than the lamellar walls [49]. The amount of magnetic material added to those TiO_2 and ZrO_2 slurries (up to 9 wt.% Fe_3O_4 particles) may have contributed to enhanced UCS values in the y-axis, which may help explain why similar trends were not observed in this work. The surface magnetized Al_2O_3 particles used in this work underwent chaining that led to observable lamellar wall alignment in the scaffold center at 75 mT for 350 nm scaffolds and 150 mT for 225 nm scaffolds. The extent of particle chaining that occurred between magnetized particles depended on particle size and thermodynamic variables (temperature, concentration) that affect aggregation and time evolution for chain formation before ice nucleation during freeze casting [56, 57, 71]. Exploration of these three factors will continue with further magnetic freeze casting experimental work.

Figure 10. Lamellar wall alignment within the scaffold center as a function of magnetic field strength and magnetized particle size. The schematic indicates the extent of particle chaining (orange line) leading to lamellar wall alignment in the scaffold center (dotted box) for each magnetized alumina particle size at varying magnetic field strength. Lower magnetic field strength produced no lamellar wall alignment within the scaffold center for smaller particles (dotted gray box). A greater degree of particle chaining for larger particles led to more lamellar wall alignment, although a stronger magnetic field caused that alignment to be near the magnet poles instead of along the horizontal axis within the scaffold center.

The schematic diagrams in [Figure 10](#) summarize how particle chaining (orange lines) leads to lamellar wall alignment in the scaffold center (dotted box), or not (dotted gray box), for each magnetized particle size at varying magnetic field strengths. For the 225 nm particles, chaining initiated by greater magnetic field strength (150 mT) overcame the thermal agitation force within the slurry, resulting in partially aligned lamellar walls within the scaffold center. For 350 nm particles with greater magnetic moment than 195 nm or 225 nm particles ([Figure 6](#)), more lamellar wall alignment occurred along the y-axis in the scaffold center at 75 mT, as compared to a magnetic field that was too strong (150 mT).

4. CONCLUSIONS

Freeze casting was carried out for the first time with varying surface-magnetized alumina (Al_2O_3) particle sizes (195, 225 and 350 nm) and magnetic fields (0, 75 and 150 mT) applied perpendicular to the ice growth direction. This new method provides an avenue for examination of physical processes that affected particle magnetic chaining and lamellar wall alignment in sintered porous scaffolds. Conclusions obtained from this experimental work include:

- A mean number distribution for each particle type determined by the dynamic light scattering (DLS) technique, and applied in combination with magnetometer data for each magnetized particle

size, indicated magnetic moment was higher for larger magnetized particles. Particle chaining, estimated from the magnetic coupling parameter $\Gamma > 1$, led to lamellar wall alignment in the scaffolds.

- Pore area and lamellar wall thickness values increased with increasing particle size. Increasing the magnetic field strength slightly increased lamellar wall thickness for only the largest particles (350 nm), which had the largest magnetic moment and were most susceptible to particle chaining.
- Scanning electron microscopy characterization of the sintered scaffold center indicated the highest lamellar wall alignment for 350 nm particles at 75 mT, even though only $\approx 20\%$ of the larger particles had $\Gamma > 1$. An increase in the compressive Young's modulus ($\approx 100\%$) and strength ($\approx 20\%$) in the magnetic field direction was found over scaffolds prepared without an applied magnetic field.
- Both the particle size and magnetic field strength need to be judiciously selected to optimize the mechanical properties. Larger particles produce more alignment and thicker lamellar walls thereby increasing the Young's modulus and strength. Even with the weak magnetic fields used in this study, the highest field produced non-parallel flux lines during freezing, resulting in angled lamellar walls that decreased the mechanical properties.
- Previous work on magnetic freeze casting used a heterogeneous slurry of magnetite particles mixed with oxide ceramic particles to align lamellar walls and mineral bridges. This work extends functionality of the process to include any materials that are surface magnetized.

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